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Iron Manganites Synthesis by the Soft Chemistry Method

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ABSTRACT

The iron manganites $\text{Fe}_x\text{Mn}_{(3-x)}\text{O}_4$ synthesis by soft chemistry method have been studied. The main difficulty is to obtain single phase spinel with high Mn content ($0.4 < x < 1.3$). Oxalate precursor powders of these materials with controlled shape and nanoscopic size have been prepared. The precursors are then heat treated with a $\text{H}_2/\text{H}_2\text{O}/\text{N}_2$ gas mixture at low temperature. The resulting stoichiometric spinels are metastable phases with high specific surface area and are highly reactive toward oxygen. Therefore, these oxide can be oxidized in air at low temperature in order to produce mixed valence defect manganites $\text{Fe}_x\text{Mn}_{(3-x)}\text{O}_{4+\delta}$ with a good reproducibility on the oxygen content. Although, some problems persist for the higher Mn contents, as the oxygen partial pressure for the reduction must be controlled precisely in order to produce the stoichiometric spinel at low temperature. The development of a low temperature reduction system, with oxygen partial pressure controlled by oxygen electrochemical pumping, is in progress.

INTRODUCTION

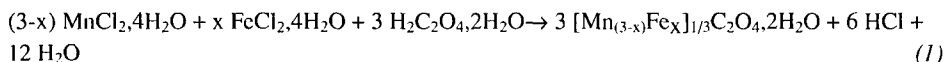
Manganese iron oxides with spinel structure has applications in magnetic recording media and electronic devices. Previous works carried on in our Laboratory have shown that it is possible to enlarge the well known properties of these materials, using metastable nanoparticles synthesized by soft chemistry at low temperature [1, 2]. Recently, the interest of these materials has greatly increased with the discovery of hard magnetic properties in metastable manganese ferrites. These properties are due to the distortion of the Mn^{3+} cations in the spinel structure by the Jahn-Teller effect [3]. The same bulk ferrites (without Cobalt) are well known to be soft magnetic materials. Moreover, magneto resistance effects have been found in similar spinel phases [4].

The aim of this work is to improve the synthesis of iron manganites $\text{Mn}_{(3-x)}\text{Fe}_x\text{O}_4$, using thermodynamical approach and a new experimental setup. First, we describe precisely the synthesis method ("soft chemistry") to obtain nanosized particles with controlled shape. Different characterizations of the precursor and the oxide powders are presented. We point out the difficulties to prepare stoichiometric oxides powders with high Mn content at low temperature, and present a new experimental process to overcome these difficulties. The phase diagram of the Fe/Mn/O system [5] shows that the spinel phase can be obtained in air at temperature above 950°C. Only a few works have been published on the synthesis of this stoichiometric spinel at low temperature [3,6,7]. Probably, the difficulty to obtain the stoichiometric spinel at low temperature is due to, the need of a better control of the reduction atmosphere, the weak crystallinity of the samples and the immiscibility gap described by Masson [8] for the natural "wredenburgite".

EXPERIMENTAL

Synthesis

The preparation of $Mn_{(3-x)}Fe_xO_4$ is done by a soft chemistry process [9]. The precursors are mixed manganese iron oxalate obtained by the co-precipitation of manganese and iron chlorides with oxalic acid, according to Eq.(1):



The chemical and the kinetic parameters of the reaction have to be well controlled. The metallic salts are dissolved in a mixed water, hydrochloric acid and ethylene glycol solution. The oxalic acid is dissolved in a 2-propanol solution with a concentration equal to the solubility limit at room temperature in this alcohol. The dissolution has to be made just before the precipitation in order to prevent the formation of an ester. The solution containing the salts, is quickly poured in the acid solution with a peristaltic pump. The pump is used to increase the saturation of the solution in order to favor the germination versus grain growth and to increase the number of germination sites. Such precipitation environment, with low dielectric constant allows the synthesis of mixed small size oxalate particles [10].

The precipitates are filtered, washed with distilled water in order to eliminate the remaining chlorides (tested by silver nitrate), washed by ethanol and dried overnight at 80°C. The powder is then grinded and sieved.

The next step of the process is the thermal decomposition of the oxalate precursor. The heating rate has to be low in order to keep the particle morphology (pseudomorphic transformation). Then the phase is reduced to obtain the stoichiometric spinel. The heat treatment of reduction is performed under a $H_2/N_2/H_2O$ mixture (flow rate ratio of 1%/49%/50% respectively) at 300°C for 5 hours. Then the samples are treated at 560°C for 2 hours in nitrogen in order to increase the crystallinity.

Analysis

A SIEMENS D501 diffractometer, equipped with a SiLi counter using $Cu_{K\alpha}$ radiation ($\lambda=0.15418$ nm) was used for the XRD analysis. Chemical analyses were performed by plasma emission spectrometry. TEM observations and microprobe analysis were made by a JEOL 2010 with a video acquisition card. The UTHSCSA ImageTool software has permitted to carry on the image analysis for granulometric distribution for a minimum of 100 particles.

Thermogravimetric analysis (TGA) was performed using a SETARAM TAG 24 apparatus and DTA by a SETARAM TAG92. Magnetic measurements have been done at room temperature with a hysteresismeter M2000 (S2IS), which allows a maximum applied magnetic field of 25 kOe. Samples were packed with a density of about 0.5 g/cm^3 .

RESULTS AND DISCUSSION
Precursor oxalate powders

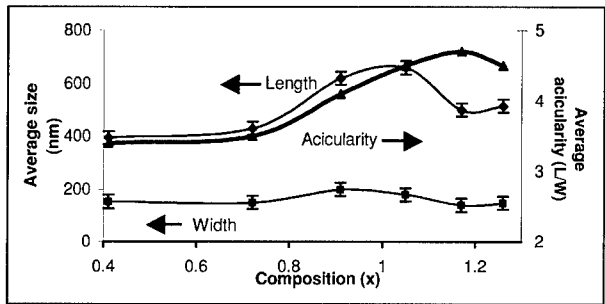


Figure 1 : Morphological evolution of the $(\text{Mn}_{(3-x)}\text{Fe}_x)_{1/3}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ oxalate as a function of composition

The oxalate particles obtained have a needle-like shape for the whole composition. The particles length and width have been determined for the different compositions (see figure 1). The size of the needles slightly changes with the composition. When the iron content varies from 0.4 to 1 the particles length increases from 400 to 600 nm. For the richer iron content, the length decreases again. The granulometric distribution shows a monomodal distribution for all the samples. These analyses prove that the particles morphology is controlled, but can slightly change with the Mn content.

The XRD patterns indicate (see figure 2) that the oxalate crystallize in the β iron oxalate structure described by Deyrieux [11]. The variation of the cell parameters is characteristic of a solid solution accorded to Vegard's law. When the concentration of manganese is high ($x < 0.9$) a small amount of manganese oxalate α is detected. However, the granulometric distribution is monomodal and electronic probe analysis shows an increasing Mn content at the edge of the particles. Therefore, the secondary phase observed is due to heterogeneous secondary germination, located at the edge of the particles.

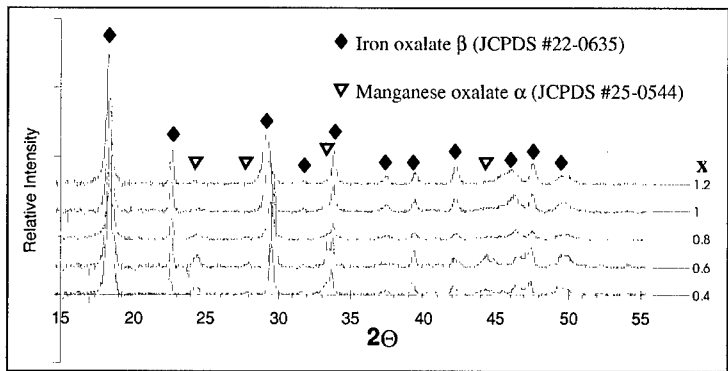


Figure 2: X-ray diffraction pattern of $(\text{Mn}_{(3-x)}\text{Fe}_x)_{1/3}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

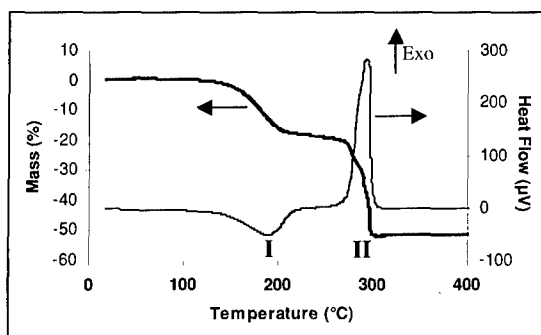
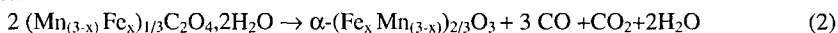


Figure 3: Thermogravimetric analysis of $(\text{Mn}_{1.7}\text{Fe}_{1.3})_{1/3}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

The thermogravimetric analysis in air indicates that the decomposition takes place in two steps for the whole composition (see figure 3). The first step (I) is endothermic and corresponds to the dehydration of two water molecules. The second step (II) is exothermic and is attributed to the decomposition of the oxalate with the release of three moles of CO and one of CO_2 , according to:



For the whole composition, the stable phase in air at 600°C is $\alpha\text{-(Mn}_{(3-x)}\text{Fe}_x)_{2/3}\text{O}_3$, so a reductive atmosphere should be used in order to obtain the spinel phase.

The exact description of the thermal treatment is given in the experimental procedure. The oxide particles have a stick shape (see figure 4). This observation indicates that the transformation is pseudomorphic. The size of the crystallite is approximately 50 nm length and 25 nm width. This shape anisotropy is well known to favour an increase in coercive field [12].

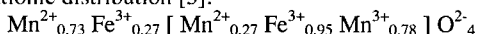
The synthesized oxides are very reactive with oxygen due to their high division state ($S_w \approx 30 \text{ m}^2/\text{g}$). Then, the cations in the spinel structure can be oxidized in air, even at low temperature ($T \sim 200^\circ\text{C}$). The oxidation treatment leads to vacancy phases with mixed valences. Because the oxides are reactive enough, each cation can be oxidized at a given temperature [13]. Then, the analysis of the derivative thermogravimetric analysis signal can be used to quantify the cation content on the tetragonal and the octahedral sites of the spinel structure.



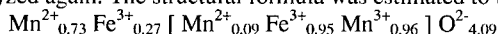
Figure 4 : TEM image of $\text{Mn}_{1.7}\text{Fe}_{1.3}\text{O}_4$

Cationic distribution and magnetic properties

This analysis has been performed on the stoichiometric spinel of composition $x = 1.3$ and gives the following cationic distribution [3]:



This cationic distribution is closed to the cationic distribution of an oxide of same composition, made at high temperature ($T=1100^\circ\text{C}$) and analyzed by Mossbauer technique [14,15]. The coercive field of the stoichiometric spinel prepared for our work, was 100 Oe ($\sim 0.8 \text{ kA.m}^{-1}$). This stoichiometric spinel phase has been oxidized for 2 hours at 275°C in air and quenched, then analyzed again. The structural formula was estimated to be:



At this temperature, only the Mn^{2+} ions in octahedral sites have been oxidized into Mn^{3+} ions. The coercive field was measured at 2500 Oe ($\sim 200 \text{ kA.m}^{-1}$), is closed to the coercive field determined by A. Agnoli [3].

Thermodynamic calculations for a new reduction process

Finally, thermodynamic calculations has been done on the pure phases of the Fe-Mn system in order to better understand the difficulties to synthesize stoichiometric spinel phases. Thermodynamic data has been collected from Fritsch et al. [16] for the Mn-O system, Laberty et al. [17] for the Fe-O system and from Knacke et al. [18] for the other data.

Calculation results are presented on an Ellingham diagram (Figure 5). The stability domain of the single bulk oxides and the partial pressure of air, nitrogen and the $\text{H}_2/\text{N}_2/\text{H}_2\text{O}$ gas mixture are reported. The partial pressure of the gas mixture is located in the stability domain of Fe_3O_4 , so this process is well adapted to obtain pure stoichiometric iron spinel even with low Mn content. It is confirmed with the diagram of the stability region of MnFe_2O_4 versus oxygen [19].

However, this gas mixture is also located in the stability domain of the wurstite MnO . Therefore, with higher Mn content the wurstite phase appears as a second phase during the reduction process. For high Mn content, the oxygen partial pressure should be around 10^{-20} atm. at low temperature ($T \sim 500^\circ\text{C}$). The $\text{H}_2/\text{N}_2/\text{H}_2\text{O}$ mixture can't be used to produce this stoichiometric spinel at low temperature, because the water content in the gas should be huge compared to nitrogen content to prevent wurstite formation during the process. For the same reason, it is difficult to use a CO/CO_2 mixture.

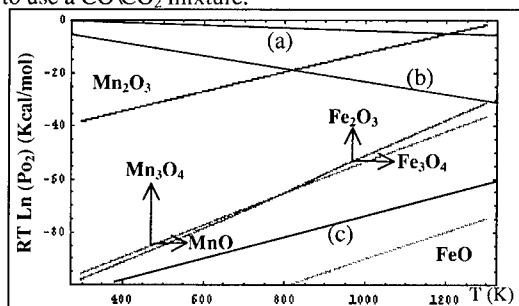


Figure 5: Calculated Ellingham diagram of the Mn-Fe system, oxygen partial pressure of air (a), nitrogen (b) and the 1% $\text{H}_2/49\% \text{N}_2/50\% \text{H}_2\text{O}$ mixture (c)

A new reduction process has been thought to produce the correct gas mixture: the electrochemical oxygen pump [20]. Previous studies dedicated to this electrochemical oxygen pump have shown that it is possible to create reducing atmospheres with 0.2 atm $<P_{O_2}<10^{-20}$ atm using a starting gas containing a few content of O_2 , H_2 or CO [21].

CONCLUSIONS

Needle shape manganese iron oxides $Mn_{(3-x)}Fe_xO_4$ powders have been synthesized by a "chimie douce" technique. This process allows to control perfectly the morphology and the size of the particle powder. The coercive field of an oxide of composition $x = 1.3$ with such characteristics was measured at 2500 Oe. The difficulty to produce higher Mn content spinel can be explained by the thermodynamical behaviour of these oxides. A new device, using electrochemical oxygen pump is in progress of development and it is believed that it should be well adapted to produce high Mn content stoichiometric spinel with a good reproducibility.

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